PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : B01J 23/52, H01M 4/90, 8/06 — A1

(11) International Publication Number: WO 00/13791

(43) International Publication Date: 16 March 2000 (16.03.00)

(21) International Application Number: PCT/IB99/01495

(22) International Filing Date: 2 September 1999 (02.09.99)

(30) Priority Data:
98/5243 7 September 1998 (07.09.98) ZA

(71) Applicant: ANGLO AMERICAN RESEARCH LABORATORIES (PROPRIETARY) LIMITED [ZA/ZA]; 44 Main Street, 2001 Johannesburg (ZA).

(72) Inventors: GRIGOROVA, Bojidara; 52 Morsim Road, Hyde Park, 2196 Sandton (ZA). MELLOR, John; 22 Bedford Avenue, Craighall Park, 2196 Johannesburg (ZA). TUMILTY, James, Anthony, Jude; 7B Palo Alto, First Avenue, Rivonia, 2128 Sandton (ZA).

(74) Agents: GILSON, David, Grant et al.; Spoor and Fisher, P.O. Box 41312, 2024 Craighall (ZA).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.

(54) Title: GOLD CATALYST FOR FUEL CELL

(57) Abstract

A fuel cell comprises two electrodes separated by an electrolyte for conversion of a fuel and an oxidant to a reaction product. The electrode or electrodes include a catalyst comprising an oxide support preferably being a mixture of zirconium oxide and cerium oxide, having gold captured thereon in catalytically effective form. The fuel is methanol or methane.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

GOLD CATALYST FOR FUEL CELL

BACKGROUND OF THE INVENTION

This invention relates to fuel cells.

A fuel cell is a device for continuously converting chemical energy into direct current electricity. The cell consists of two electronic conductor electrodes separated by an ionic conducting electrolyte with provision for the continuous movement of fuel, oxidant and reaction product into and out of the cell. The fuel may be gaseous or liquid; the electrolyte liquid or solid; and the oxidant is gaseous. The electrodes are solid, but may be porous and contain a catalyst. Fuel cells differ from batteries in that electricity is produced from chemical fuels fed to them as needed.

Fuel cell technology has lagged behind that of the development of hot combustion engines, yet promises to be a contender in the sphere of small scale power generation. There are several reasons for this. For example, fuel cells can be inherently zero-emission power sources and there are a wide variety of potential fuels and oxidants available. Further, when a fuel cell driven vehicle is stationary, no fuel is used. Problems limiting the viability of fuel cells are present. For example, a suitable fuel must be available at a competitive price. Further, a suitable and cost effective catalyst is still unavailable. Base metals have been tried as catalysts but degradation of the catalyst often occurs. Platinum group metals have also been used, but sufficiently high activity at low loading has not yet been achieved.

SUMMARY OF THE INVENTION

According to a first aspect of the invention there is provided a fuel cell comprising two electrodes separated by an electrolyte for conversion of a fuel and an oxidant to a reaction product which fuel cell is characterised in that the electrode or electrodes include a catalyst comprising an oxide support having gold captured thereon in catalytically effective form, and in that the fuel is methanol or methane.

According to a second aspect of the invention there is provided a catalyst comprising an oxide support having gold captured thereon in catalytically effective form, for use in a fuel cell comprising two electrodes separated by an electrolyte for conversion of a fuel selected from methanol or methane, and an oxidant, to a reaction product.

According to a third aspect of the invention there is provided a method of oxidising methanol or methane as a fuel for a fuel cell which is characterised in that the oxidation takes place in the presence of a catalyst comprising an oxide support having gold captured thereon in catalytically effective form.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1A and 1B are graphs of methane oxidation at various temperatures, with Figure 1B illustrating the results of a repeat test;

BEST AVAILABLE COPY

Figures 2A and 2B are graphs of methane oxidation at various temperatures, with Figure 2B illustrating the results of a repeat test of the catalyst K5(3); and

Figure 3 is a graph comparing the activity of a catalyst of the invention compared to the activity of a platinum catalyst, for methanol reformation

DESCRIPTION OF EMBODIMENTS

Examples of preferred gold based catalysts useful in fuel cells are those disclosed in United States Patent 5,759,949, EP 0789621 and WO 97/45192, which are incorporated herein by reference..

One preferred form of the gold-based catalyst comprises an oxide support, preferably a mixture of cerium and zirconium oxide, a transition metal oxide, preferably cobalt oxide, to which the gold is complexed and optionally also containing an oxide of titanium or molybdenum.

The oxide support is preferably present in the catalyst in an amount of at least 50% by mass of the catalyst, and generally at least 60% by mass of the catalyst. The cerium oxide will generally constitute at least 50% by mass of the mixture of zirconium oxide and cerium oxide. The preferred mass ratio of cerium oxide to zirconium oxide is in the range 5:1 to 2:1, typically about 3:1.

The catalyst contains gold in catalytically effective form. This form will vary according to the nature of the catalyst.

The concentration of the gold will generally be low, i.e 2% or less by mass of the catalyst.

As indicated above, the catalyst preferably also contains a transition metal in oxide form, examples being ferric oxide, or preferably cobalt oxide.

Fuels which have been found to be particularly effective and useful in the practice of the invention are methane and methanol.

The gold-based catalyst has application for both electrochemical and chemical oxidation reactions taking place in a fuel cell.

An example of a fuel cell in which a gold-based catalyst may be used is that which involves the total or partial oxidation of methane as the fuel. The ability of a number of gold-based catalysts of the type described in WO 97/45192 were tested in the oxidation of methane. The compositions which were used are set out in Table 1.

Table 1: Compositions of the catalysts tested for total methane oxidation

Code	K1	K2	K5(2)	K5(3)
Active Component	1.0% Au 1.0% Co	1.0% Au 1.0% Co	1.0% Au 1.0% Co	1.0% Au 1.0% Co
Support				
CeO_2	38%	49%	44%	42%
CeO_2/ZrO_2	47.5%	40%	38%	40%
TiO_2	9.5%	10%	15%	15%
Balance other oxides	5.0%	1.0%	3.0%	2.0%

The tests were conducted with 0.25% methane (see Figure 1), and 2.5% methane (see Figure 2), with the balance air. The hourly space velocity of the gas mixture was 12 000h^{-1}.

BEST AVAILABLE COPY

Samples K1 and K2 were tested in 0,25% methane, balance air, to 500°C and the samples K5(2) and K5(3) were tested at 600°C. After each test, the samples were cooled in air to room temperature and re tested.

It was found that sample K5(3) gave the highest methane conversion and is stable at a temperature of 600°C.

Samples K1, K2, K5(2) and K5(3) were also tested in 2,5% methane, balance air, to 600°C.

Sample K5(3) was cooled from 600°C in air to room temperature and re-tested in the reaction mixture to 600°C to evaluate catalyst stability in the higher concentration of methane test gas.

It was found that the catalyst performed well in the higher concentration of methane and showed good durability.

The gold-based catalyst may also be used in a direct methanol fuel cell. Methanol is considered as a fuel of choice because of its compatibility with existing distribution networks. The results of testing carried out show that the gold based catalyst is very active for methanol oxidation at low temperature. This is of significance as a major limitation of the commercialisation of methanol fuel cell has been the lack of catalyst for methanol oxidation at temperatures lower than 100°C.

Various gold-based catalysts of the type disclosed in WO 97/45192 were tested in their ability to catalyse the oxidation of methanol. The catalysts K2 and K5(2) were tested for methanol oxidation.

Sample K2 was evaluated in a reaction mixture containing 6.5% methanol, balance air, whilst sample K5(2) was tested in mixtures containing 6.5% and 11% methanol, balance air.

Experiments 1 and 2 were performed by pumping the required amount of liquid methanol into a vaporiser. In experiments 3, a bubbler was used to introduce methanol as this method proved to give more consistent and homogeneous reactant mixtures under the operating conditions. The operating conditions under which each sample was tested is presented in the results. Reactant and product analyses were obtained using gas chromatography.

RESULTS

For experiment 1 and 2 liquid methanol at the appropriate pump rate was fed into the vaporiser. The samples were cooled to 50°C prior to the start of the reaction.

Experiment 1

Sample:	K2
Reactant composition:	6,5% CH_3OH, balance air
Space Velocity:	20 000h^{-1}
Flowrate:	200ml/min
Sample Mass:	0,6g

BEST AVAILABLE COPY

Table 1: Activity of Sample K2 for methanol oxidation as a function of temperature

Temperature (°C)	CH_3OH Conversion (%)	Residual Products CO(%)
50	18.8	0
100	65.6	0

Experiment 2

Sample: K5(2)

Reactant composition: 6,5% CH_3OH, balance air

Space Velocity: 62 600h^{-1}

Flowrate: 313ml/min

Sample Mass: 0,3g

Table 2: Activity of Sample K5(2) for methanol oxidation as a function of temperature

Temperature (°C)	CH_3OH Conversion (%)	Residual Products CO(%)
50	99.7	0
100	99.8	0

For experiment 3 the samples were cooled to room temperature prior to starting the reaction. Methanol was introduced at room temperature by bubbling air through the liquid methanol bubbler.

Experiment 3

Sample: K5(2)

Reactant composition: 11% CH_3OH, balance air

Space Velocity: 57 600h^{-1}

Flowrate: 96ml/min

Sample Mass: 0,1g

Table 3: Activity of Sample K5(2) for methanol oxidation as a function of temperature

Temperature (°C)	CH_3OH Conversion (%)	Residual Products CO(%)
44	99,4	0
50	100	0
100	100	0

The activity of a gold catalyst of the invention for methanol reformation was compared to that of a platinum catalyst and was shown to be superior, as is indicated in Figure 3.

CLAIMS

1 A fuel cell comprising two electrodes separated by an electrolyte for conversion of a fuel and an oxidant to a reaction product is characterised in that the electrode or electrodes include a catalyst comprising an oxide support having gold captured thereon in catalytically effective form, and in that the fuel is methanol or methane.

2 A fuel cell according to claim 1 wherein the catalyst comprises an oxide support being a mixture of zirconium oxide and cerium oxide having captured thereon gold in catalytically effective form, the oxide support being present in the catalyst in an amount of at least 50% by mass of the catalyst.

3 A fuel cell according to claim 2 wherein the oxide support is present in the catalyst in an amount of at least 60% by mass of the catalyst.

4 A fuel cell according to claim 2 or claim 3 wherein the cerium oxide constitutes at least 50% by mass of the mixture of zirconium oxide and cerium oxide.

5 A fuel cell according to any one of claims 2 to 4 wherein the mass ratio of cerium oxide to zirconium oxide is in the range 5:1 to 2:1.

6 A fuel cell according to any one of claims 1 to 5 wherein the catalyst also contains a transition metal in oxide form.

7 A fuel cell according to claim 6 wherein the transition metal oxide is selected from cobalt oxide and ferric oxide.

8 A fuel cell according to claim 7 wherein the gold is associated with the transition metal oxide.

9 A fuel cell according to any one of claims 1 to 8 wherein the catalyst includes an oxide of titanium or molybdenum.

10 A catalyst comprising an oxide support having gold captured thereon in catalytically effective form for use in a fuel cell comprising two electrodes separated by an electrolyte for conversion of a fuel selected from methanol or methane, and an oxidant to a reaction product.

11 A catalyst according to claim 10 wherein the catalyst comprises an oxide support being a mixture of zirconium oxide and cerium oxide having captured thereon gold in catalytically effective form, the oxide support being present in the catalyst in an amount of at least 50% by mass of the catalyst.

12 A catalyst according to claim 11 wherein the oxide support is present in the catalyst in an amount of at least 60% by mass of the catalyst.

13 A catalyst according to claim 11 or claim 12 wherein the cerium oxide constitutes at least 50% by mass of the mixture of zirconium oxide and cerium oxide.

14 A catalyst according to any one of claims 11 to 13 wherein the mass ratio of cerium oxide to zirconium oxide is in the range 5:1 to 2:1.

15 A catalyst according to any one of claims 10 to 14 wherein the catalyst also contains a transition metal in oxide form.

16 A catalyst according to claim 15 wherein the transition metal oxide is selected from cobalt oxide and ferric oxide.

17 A catalyst according to claim 16 wherein the gold is associated with the transition metal oxide.

18 A catalyst according to any one of claims 10 to 17 wherein the catalyst includes an oxide of titanium or molybdenum.

19 A method of oxidising methanol or methane as a fuel for a fuel cell is characterised in that the oxidation takes place in the presence of a catalyst comprising an oxide support having gold captured thereon in catalytically effective form.

20 A method according to claim 19 wherein the catalyst comprises an oxide support being a mixture of zirconium oxide and cerium oxide having captured thereon gold in catalytically effective form, the oxide support being present in the catalyst in an amount of at least 50% by mass of the catalyst.

21 A method according to claim 20 wherein the oxide support is present in the catalyst in an amount of at least 60% by mass of the catalyst

22 A method according to claim 20 or claim 21 wherein the cerium oxide constitutes at least 50% by mass of the mixture of zirconium oxide and cerium oxide.

23 A method according to any one of claims 20 to 22 wherein the mass ratio of cerium oxide to zirconium oxide is in the range 5:1 to 2:1.

24 A method according to any one of claims 19 to 23 wherein the catalyst also contains a transition metal in oxide form.

25 A method according to claim 24 wherein the transition metal oxide is selected from cobalt oxide and ferric oxide.

26 A method according to claim 25 wherein the gold is associated with the transition metal oxide.

27 A method according to any one of claims 19 to 26 wherein the catalyst includes an oxide of titanium or molybdenum.

Fig 1A

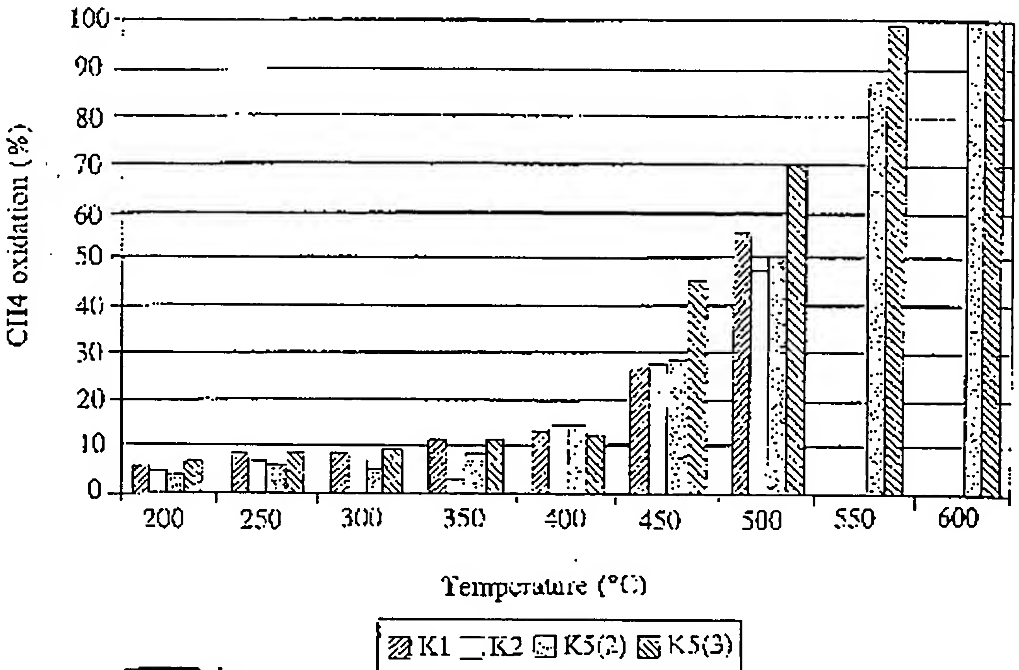

100
90
80
70
60
50
40
30
20
10
0
CH4 oxidation (%)
200
250
300
350
400
450
500
550
600
Temperature (°C)
K1
K2
K5(2)
K5(3)

Fig 1B

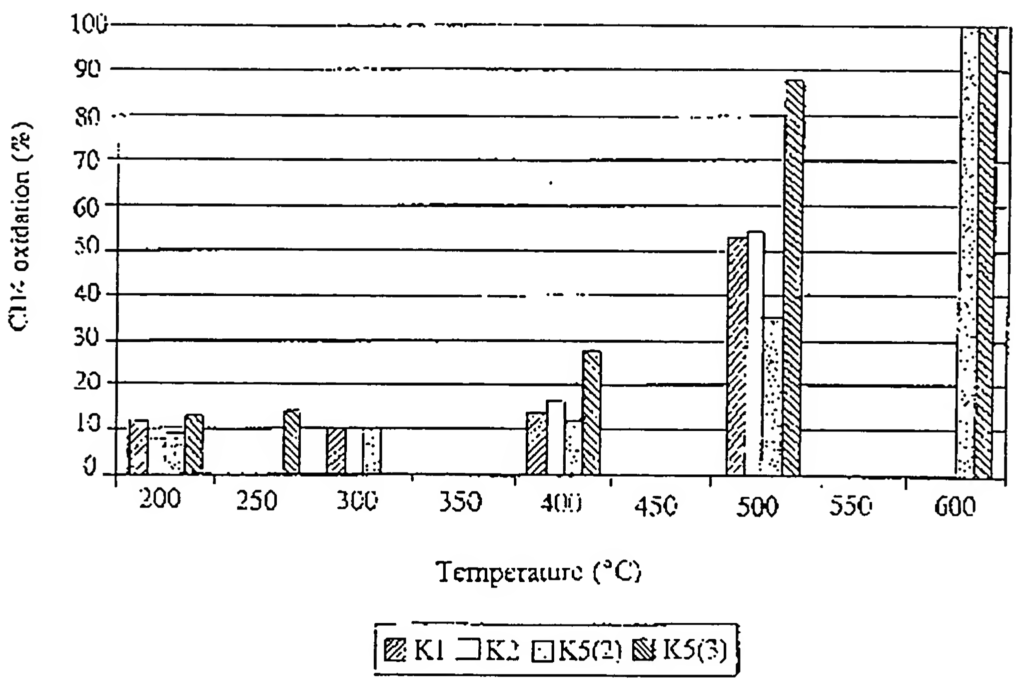

100
90
80
70
60
50
40
30
20
10
0
CH4 oxidation (%)
200
250
300
350
400
450
500
550
600
Temperature (°C)
K1
K2
K5(2)
K5(3)

FIG 2A

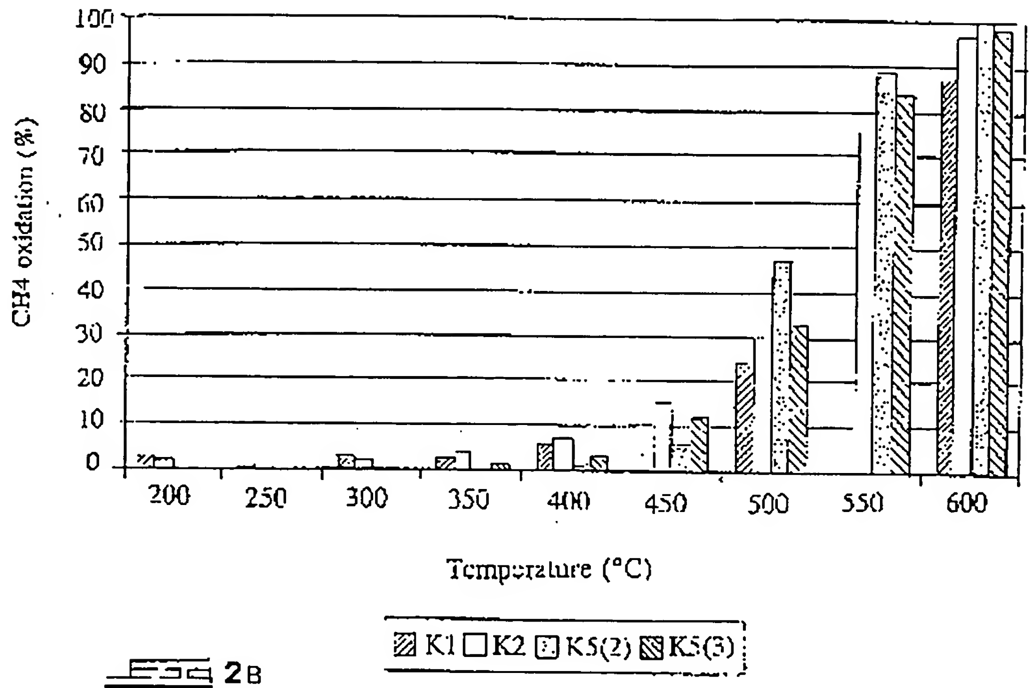

CH4 oxidation (%)
100
90
80
70
60
50
40
30
20
10
0
200
250
300
350
400
450
500
550
600
Temperature (°C)
K1 K2 K5(2) K5(3)

FIG 2B

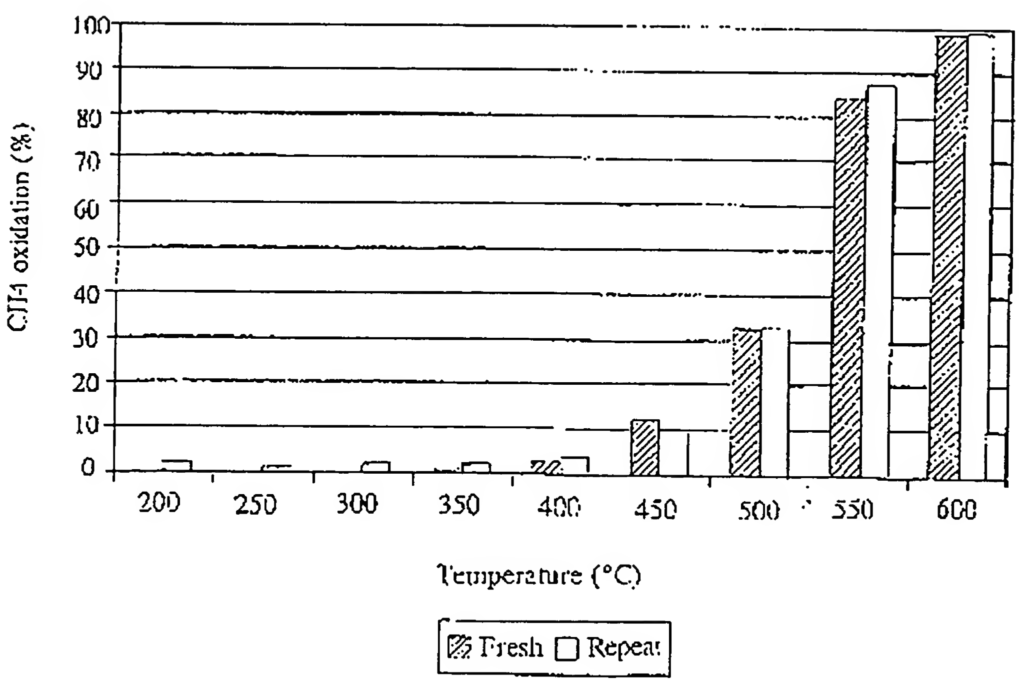
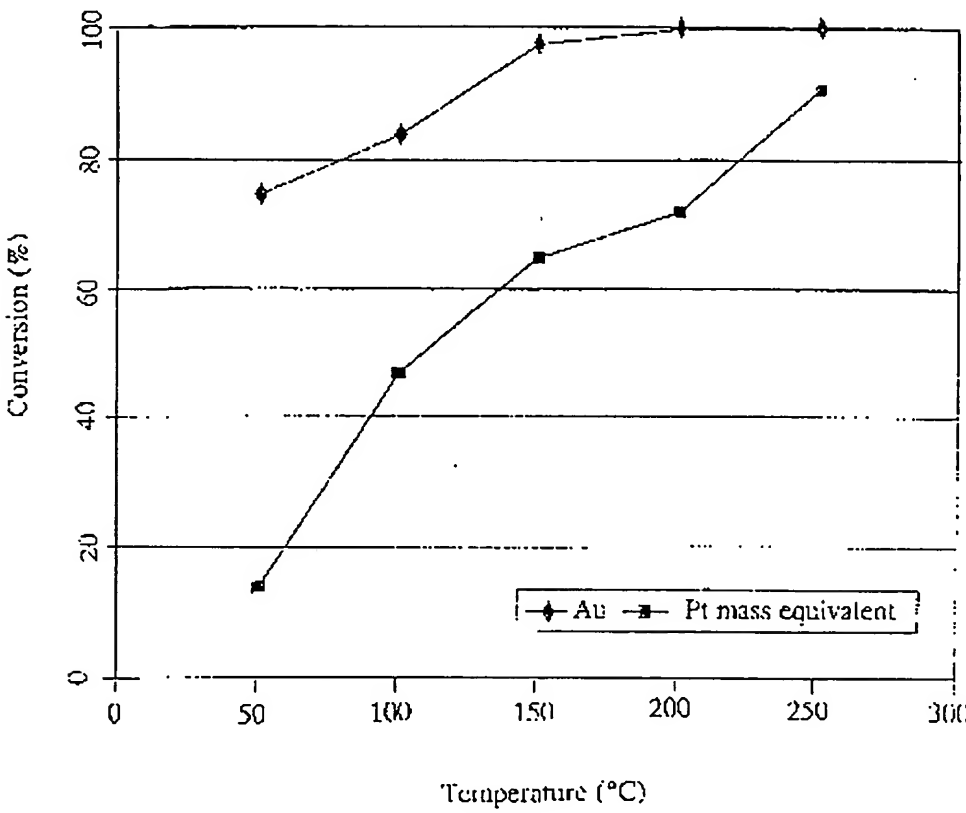

CH4 oxidation (%)
100
90
80
70
60
50
40
30
20
10
0
200
250
300
350
400
450
500
550
600
Temperature (°C)
Fresh Repeat

FIG 3


Conversion (%)
100
80
60
40
20
0
0
50
100
150
200
250
300
Temperature (°C)
Au
Pt mass equivalent

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 99/01495

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J23/52 H01M4/90 H01M8/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	M HARUTA ET AL: "Low-temperature catalytic combustion of metnanol and its decomposed derivatives over supported gold catalysts" CATALYSIS TODAY, NL, AMSTERDAM, vol. 29, page 443-447 XP002092222 page 443, line R, paragraph 2 page 444, left-hand column, paragraph 4 -right-hand column, paragraph 2 ---	1,10,19
X	US 4 839 327 A (KOBAYASHI TETSUHIKO ET AL) 13 June 1989 (1989-06-13) column 1, line 61 - line 66 column 2, line 16 - line 23 column 1, line 8 - line 13 column 3, line 25 - line 28 column 7, line 20 - line 44 ---	1,10,19

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 November 1999	13/12/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Gamez, A

BEST AVAILABLE COPY

International Application No
PCT/IB 99/01495

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 331 123 A (JOHNSON MATTHEY PLC) 17 January 1990 (1990-01-17) page 2, line 1 - line 26	1,10,19
A	page 2, line 37 - line 43	2,11,20
P,X	WO 99 16546 A (LAMAN CONSULTANCY LIMITED ;TATCHEV VASSIL METODIEV (BG)) 8 April 1999 (1999-04-08) page 3, paragraph 2 - paragraph 4 page 4, paragraph 1	1,6-8, 10, 15-17, 19,24-26
A		4,13,22
P,X	WO 98 51401 A (LAMAN CONSULTANCY LIMITED ;PETROV LACHEZAR ANGELOV (BG)) 19 November 1998 (1998-11-19) page 3, paragraph 2 - paragraph 4	10,13-16
A	page 4, paragraph 3; example 1	1,4-7, 19,22-25
X	WO 96 14153 A (GRIGOROVA BOJIDARA ;PALAZOV ATANAS (ZA); MELLOR JOHN (ZA); TUMILTY) 17 May 1996 (1996-05-17) cited in the application page 2, line 12 -page 3	10-17
A	page 4, line 11 -page 5, line 5	1-8, 19-26
X	WO 95 19843 A (ANGLO AMERICAN RES LAB PTY LTD ;TUMILTY JAMES ANTHONY JUDE (ZA)) 27 July 1995 (1995-07-27) page 4, paragraph 1 - paragraph 2 page 5, paragraph 5 -page 6, paragraph 2	10,15,16
A	page 6, paragraph 4 -page 7, paragraph 1	1,6,7, 19,24,25
X	EP 0 602 865 A (JOHNSON MATTHEY PLC) 22 June 1994 (1994-06-22) page 3, line 7 - line 12 page 3, line 21 - line 27 page 5, line 44 - line 49	10,14
X	CHEMICAL ABSTRACTS, vol. 127, no. 5, 4 August 1997 (1997-08-04) Columbus, Ohio, US; abstract no. 68522, NAGANO, SHIN ET AL: "Low temperature polymer electrolyte fuel cells" XP002124178	10
A	abstract & JP 09 129243 A (TOYOTA CENTRAL RESEARCH AND DEVELOPMENT LABORATORIES, INC., JAPAN) 16 May 1997 (1997-05-16)	1,19

-/--

International Application No
PCT/IB 99/01495

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 759 949 A (MELLOR JOHN ET AL) 2 June 1998 (1998-06-02) cited in the application	10
A	column 1, line 66 -column 2, line 35	1,15,16, 19

BEST AVAILABLE COPY

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/IB 99/01495

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 4839327	A	13-06-1989	JP	1828306	C	15-03-1994
			JP	5034284	B	21-05-1993
			JP	63252908	A	20-10-1988
EP 0351123	A	17-01-1990	DE	68908639	D	30-09-1993
			DE	68908639	T	13-01-1994
			ES	2043021	T	16-12-1993
			JP	2103867	A	16-04-1990
			US	5246791	A	21-09-1993
WO 9916546	A	08-04-1999	AU	9147998	A	23-04-1999
			BG	101931	A	30-04-1999
WO 9851401	A	19-11-1998	AU	7201398	A	08-12-1998
			BG	101490	A	30-04-1999
WO 9614153	A	17-05-1996	AT	179907	T	15-05-1999
			AU	698375	B	29-10-1998
			AU	3809995	A	31-05-1996
			CN	1171063	A	21-01-1998
			DE	69509672	D	17-06-1999
			DE	69509672	T	16-09-1999
			EP	0789621	A	20-08-1997
			ES	2132728	T	16-08-1999
			JP	10509377	T	14-09-1998
			US	5895772	A	20-04-1999
			ZA	9509075	A	22-05-1996
WO 9519843	A	27-07-1995	AT	186230	T	15-11-1999
			AU	690956	B	07-05-1998
			AU	1461595	A	08-08-1995
			CA	2182003	A	27-07-1995
			EP	0741607	A	13-11-1996
			IL	112414	A	16-08-1998
			JP	9508058	T	19-08-1997
			US	5665668	A	09-09-1997
			ZA	9500584	A	04-10-1995
EP 0602865	A	22-06-1994	AU	675463	B	06-02-1997
			AU	5247493	A	30-06-1994
			CA	2111529	A	19-06-1994
			JP	6219721	A	09-08-1994
			US	5480854	A	02-01-1996
JP 9129243	A	16-05-1997	NONE			
US 5759949	A	02-06-1998	AT	154764	T	15-07-1997
			AU	669612	B	13-06-1996
			AU	6009494	A	14-09-1994
			CA	2156282	A	01-09-1994
			DE	69403953	D	31-07-1997
			DE	69403953	T	18-12-1997
			DK	684869	T	05-01-1998
			EP	0684869	A	06-12-1995
			ES	2103574	T	16-09-1997
			WO	9419092	A	01-09-1994
			IL	108635	A	30-09-1997
			JP	8506992	T	30-07-1996

Form PCT/ISA/210 (patent family annex) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/IB 99/01495

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5759949 A		ZA 9401123 A	30-08-1994

BEST AVAILABLE COPY

Form PCT/ISA/210 (patent family annex) (July 1992)